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Influence of ZrO₂ particles on the optical properties of pc-LEDs

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Abstract

Experimental and modeling progress and results aiming to increase the color uniformity of hemisphere-type pcW-LEDs are proposed. By adding micrometric zirconia particles, the light scattering is enhanced, that induces a decrease of phosphor necessary to obtain a specific CCT. The optical model is able to determine the optical properties (CCT, angular CCT distribution, chromaticity and packaging efficiency) in a hemisphere LED for various amount of YAG-phosphor and ZrO₂-zirconia particles. Based on previous process, the work is in the first step to fit the effective radius and refractive index that will be implemented in the optical model. In the second step, the optical model is compared with the experimental measurement to determine the absorption coefficient and conversion efficiency of a package of silicone resin containing phosphor and zirconia. Finally, the model, confirmed by selected experimental results, allows determining the optical properties of any kind of package that lead to a CCT emission ranging from 4500K to 6500K. The analysis of these data is interpreted by comparing, for a specific CCT, the phosphor loss, the packaging efficiency and the angular distribution of CCT. The results show that if the effort is targeted on one of the previous parameters, there is always a counterpart on the other ones. Increasing the color uniformity will induce to decrease the packaging efficiency.

Keywords: Diffuser, YAG, packaging, CCT, spatial uniformity, phosphor loss

Introduction

Light-emitting diodes (LEDs) are now widely used as solid state light sources for indoor and outdoor applications [1]. Its robustness, low-cost, high efficiency and environmentally friendly components materials make this device an ideal replacement for light bulbs and discharge lamps [2]. Most of the white LEDs are based on the combination of a blue die (InGaN) and a phosphor which down-convert a part of the blue beam into a yellow emission [3]. In this case, the technique is called phosphor-converted white LED (pcW-LED) [4].

Many efforts were performed these recent years to improve the extraction of light on a pcW-LED device [6]. The influence of packaging was analyzed, by comparing conformal, hemisphere, remote phosphor design, etc [6]. An important point was to understand the influence of the phosphor particle size and the particle number [7]. This last parameter is one of the most important key factors on the light output flux and the Correlated Color Temperature (CCT), in addition of the recycling effect of phosphor particle [8]. This issue was demonstrated experimentally and also by modeling, using an Monte Carlo ray tracing process, taking into account the scattering effect, the absorption coefficient, the conversion efficiency, the geometry of the packaging and the refractive index of the phosphor and the polymer of the package [9]. This method was successfully performed on various phosphors (YAG, Silicate, and green YAG) [10]. The reabsorption of the phosphor emission by the phosphor itself was also analyzed, allowing simulating perfectly any kind of pcW-LED optical properties [11].

The color uniformity is also an important issue [12], which is not often taken into account in the literature. The usual consequence of a central and directional blue source combined with phosphor particles having an isotropic scattering is called the yellow ring phenomenon [13]. There is a more intense blue light (high CCT) in the normal direction of the die, and more yellowish light in the peripheral directions. The angular CCT deviation (ΔCCTD) can reach 3000 K in non-optimized recipes [14]. For large size applications used to illuminate an important surface, this issue became drastic. Some papers deal with solution to decrease the ΔCCTD ; by modifying the conformal coating [15], using specific lens [16], shaping the phosphor layer [17]. Some complex solutions were also proposed, like using a patterned sapphire substrate [18] or a graded refractive index multilayer phosphor package [19]. The influence of all this solution on the ΔCCTD has to be regarded in parallel with the influence on the output flux. It appears that the effects are not the same as a function of the CCT [20]. For high CCT, the ΔCCTD is more important due to lack of scattering effect of phosphor, compared to a low CCT device containing more phosphor. In this paper, we propose to analyze the influence of incorporation of zirconia (ZrO_2) particles, known as an efficient diffuser, into the phosphor packaging on the ΔCCTD .

Similar experiment were published by Chen et al. [21] who incorporate nano-particles of ZrO_2 and showed that their process lead to decrease the ΔCCTD . While they did not discuss about the phosphor reduction, it seems that the use of nano-particles in a remote phosphor design increase the backward scattering effect of zirconia what induces, in some case, an increase of luminous flux, essentially due to the high photon recycling. An important difficulty is that they used the luminous flux to compare the influence of ZrO_2 , without taking care of the change in CCT.

The final device used in this work is a hemisphere packaged pcW-LED, what is one of the most commercially-used recipes. Comparison between experimental and modeling results are performed and analyzed as a function of the CCT. In addition to the color uniformity, the effect of adding zirconia particles on the amount of phosphors (for the same CCT) will be analyzed.

Indeed, the amount of phosphor gets a direct influence on the thermal issue, i.e. the reliability of the lighting device [22]. Allowing decreasing the amount of phosphor may play a role on that purpose. On a more general point of view, phosphor contains rare earth element (cerium in most of the case, europium in some specific phosphor). The rare earths elements are now declared as critical raw elements [23]. Every process than can decrease the use of rare earth element will be interesting in that context.

Experimental, Modeling

The experimental process defined in this work is similar than the work performed previously on yellow emitting phosphors, green emitting phosphors taking into account the reabsorption phenomena [11], silicate-based phosphors [10], and on the influence of the particles number [8].

The elements used are

- * yellow YAG phosphor (Cool White YAG 00902 from Hung Ta Co.)
- * zirconia particles (ZrO_2 from Fisher-Bioblock, 98%)
- * silicone resin (KER-2600 (A/B) from ShinEtsu Chemical Co.

The YAG particles size is defined by a gaussian distribution from 2 to 10 μm , centered at 6 μm [8]. YAG particles get a refractive index of 1.83 and a density of 4.3 g/cm^3 . The zirconia particles are composed of some small particles (1-3 μm) and mainly bigger particles (distribution from 3 to 26 μm , centered at 12 μm). Zirconia particles get a refractive index of 2.13 and a density of 5.89 g/cm^3 . Silicone is formed by a mixture of polymer and curing agent. It is assumed in this work totally transparent, and gets a refractive index of 1.41 and a density of 1 g/cm^3 .

The first packages (YAG and zirconia incorporated into silicone) are plates of 13 mm in diameter with various thicknesses. These plates are elaborated by mixing defined amounts of YAG and zirconia particles in the silicone and then injected onto a specific mold after removing the air inside the mixture with the use of a vacuum chamber. The mold is then heated at 120°C on a hot plate during 5 min to cure the silicone.

In order to scan the influence of the plate thickness, phosphor concentration and zirconia concentration, many plates were elaborated with thickness of 0.6, 0.8, 1.0, 1.2 and 1.5 mm, YAG weight of 3, 5, 7.5 and 10%, and zirconia weight ratio of 1, 5, 10, 15%. All these parameters correspond to 64 plates. Each plate was produced three times, to be sure about the reproducibility of the measurements.

The first goal is to estimate the effective radius and refractive index in a scattering model. The effective particle size is related to the fraction obscuration and the cross-sectional area of the particle mixed with silicone. For that purpose, an experimental set-up [11] allows measuring the scattering light distribution. A He-Ne 632.8 nm laser is used as the light source. The phosphor plate is positioned in the center of the rotational stage where a power meter is measuring the scattered light. These measurements are performed for all the plates. In parallel, a model [10] using a Monte-Carlo ray tracing process combined with the Mie scattering theory is developed to simulate the light scattering for different plate thickness (Fig. 1.).

As seen in the Fig. 1, the modeling is efficient in the angle range $-160^\circ \rightarrow 160^\circ$, with the exception of the $-100^\circ \rightarrow -80^\circ$ and $80^\circ \rightarrow 100^\circ$. The results were normalized to 1 for the zero angle. An increase of the backscattered flux is observed as a function of the thickness. It is due to the Mie scattering that get more influence because of the increase of the ZrO_2 particles number. The fitting of the scattering model and the experimental measurement allows adjusting the effective refractive index and particle size of the phosphor.

The results are shown in Fig. 2.

The effective refractive index shown in Fig. 2.b. is an intrinsic parameter of the particles used in the model. The refractive index η is: $\eta = 1.77 X + 1.83$, where X is the % of ZrO_2 in the total amount of particles (YAG + zirconia). These data are obtained for various amounts of particles. These results reveal that the X parameter is the key parameter driving the optical properties, what allows getting rid of the complex influence of the plate thickness combined with the concentration of particles. $\eta = 1.83$ corresponds to the effective refractive index of the plate composed of only YAG. For $X=100\%$ (plate with only zirconia), the effective refractive index is 3.61. The refractive index is assumed to be independent of the wavelength (in the visible range) [24].

The effective particle radius ϕ is: $\phi=2.135-0.044.X-2.07 X^2$. $\phi=2.135$ correspond to the effective radius of plate containing only YAG.

The second goal is to calculate the absorption coefficient and the conversion efficiency of the plates. The absorption coefficient corresponds to the amount of blue light absorbed by the plate. This parameter is wavelength dependent [25], due to the 4f-5d transitions of cerium, and usually described by a Beer-Lambert Law: $\alpha_{\text{mm}^{-1}} = -1/\ell \cdot \ln(I/I_0)$ where I_0 is the incident light, I is the output light and ℓ is the path of light in the plate. The conversion efficiency, also wavelength dependent, is the ratio of final output energy (E_f) versus the absorbed light (E_a).

For that purpose, a blue chip (EZ-700 from Cree; 449 nm) is connected on a MCPCB board, and a black acrylic tube allows positioning the plate on the top of the device and to remote the plate from the blue die in order to reduce some thermal effect (Fig. 3.a.). The MCPCB board is connected to an efficient home-made heat dissipation to provide a stable blue light output. The black acrylic tube can be modified by various color coating (grey, white, mirror, in order to modify the reflectivity of the device to adjust the recycling effect of photon coming from the backward reflection of light from the phosphor plate). So the reflectivity is adjusted from 0 (black), 50 (grey) 85 (real rough metallic surface), 90 (white) and 100 (mirror).

Measurements are performed by placing the device on the previous set-up to characterize angular distribution, then in an integrating sphere (Sphere Optics, Ilumnia, injection current 50 mA, voltage from 2.91 to 2.95 V) to characterize the total spectral emission from 350 to 750 nm (Fig. 3. b.). The integrating sphere allows measuring the incident blue light (device without plate), then the output blue light passing through the plate and the yellow light emitted by the phosphor –Fig. 3. c..

The global result from these first measurements is that the increasing of the plate thickness or the YAG concentration leads to the increase of the yellow emission. This point was already explained by Yang et al. [8], showing that the key parameter is the phosphor particle number, that can be modified by increasing the thickness of the package or the YAG concentration. But increasing the zirconia particles seems to have a similar effect. The scattering of blue beam by the zirconia increase the efficiency of the YAG phosphor.

As described in previous papers [8, 9], the process used for optical modeling is illustrated in Fig. 4.

The model, still using the Monte Carlo ray tracing and the Mie scattering theory, simulate the output flux of blue and yellow light.

A single effective particle model is proposed, using the scattering model developed previously with the calculation of the effective refractive index and effective radius, as a function of the ZrO_2 ratio in the total amount of particle.

With various combinations of YAG and zirconia, the single effective particle model is used to determine the effective absorption coefficient and effective conversion efficiency. These last parameters are calculated as a function of the YAG concentration. In all the following experimental and simulation data, the reflectivity of the device is of 85 %, what corresponds to a real rough metallic surface.

Both the absorption coefficient and the conversion efficiency are fitted by a single value corresponding to the absorption at 449 nm and the conversion efficiency from 449 nm to 550 nm. This value is then affected to the blue die spectrum and the YAG absorption and emission spectra [11]. Final results are shown in Fig. 5.

The effective absorption coefficient concerns only the YAG amount, what is the only particles absorbing blue light. It increases with the amount of YAG particles. The effective absorption coefficient A is defined by $A=0.0086 z^2 - 0.0011z + 0.217$, where z is the weight % of YAG.

Effective conversion efficiency, as shown in the Fig. 5.b. is an intrinsic parameter of YAG. So it's not affected by the amount of YAG or zirconia, neither the thickness of the plate nor the concentration of particle. The value is determined as 0.8 ± 0.03 .

Once all these parameters are determined, the next step is to analyze the ZrO_2 influence on the real hemisphere shaping device (Fig. 6.). The die and the MCPCB board are the same than those previously used. The package is a hemisphere of 4mm in diameter cover by a silicone lens (ShinEtsu, Ker2600, 1.5 1mm thick). The refractive index of this lens is 1.41, the same refractive index than the silicone of the hemisphere, allowing extracting a maximum of light from the phosphor hemisphere. The hemisphere is elaborated by the same process than the plate, except that the mold has a different shape.

Because the modeling task was shown to be efficient and can be adjusted to various shaping [11], only some selected experiments were performed (YAG 3%, ZrO_2 5%; YAG 5%, ZrO_2 1%; YAG 5%, ZrO_2 5%; YAG 7.5%, ZrO_2 1%; YAG 7.5%, ZrO_2 5%).

The experimental measurements and the simulation allow determining the chromaticity (x, y in the CIE 1931 norm [26]), the CCT, the angular CCT distribution and the packaging efficiency (corresponding to the absorption coefficient multiply by the conversion efficiency).

A selection of experimental and simulated results is shown in the Fig. 7.

Regarding the chromaticity, the difference between experiment and simulated x and y value are less than 0.01. The packaging efficiency is in a 5% of deviation.

Discussion

With all the data collected and the modeling part, the packaging efficiency and the phosphor reduction are shown in Fig. 8.

Some chromaticity and CCT characteristics can be reached by different configuration of ZrO_2 and YAG. For a specific CCT target, the zirconia addition allows decreasing linearly the YAG amount, what is an important task of this work. For example, 6500K is obtained by a package containing 6.3% of YAG, or 3% of YAG and 11.5% of ZrO_2 . The maximum phosphor reduction is about 60%. The phosphor reduction should be higher for low CCT (where the phosphor influence is higher). But this influence is not clearly shown in the Fig. 8. where all the phosphor reduction curve are within the same range of accuracy. These results are very promising, in the context of the critical raw element rare earth [23].

However, the packaging efficiency is the weak point of such zirconia incorporation. At 5500K, the efficiency is of 64% for a YAG-only hemisphere, and 50% for the 4% of YAG and 10% of ZrO_2 configuration. The packaging efficiency is lower for low CCT, already mentioned in [8], due to the higher amount of phosphor. But in addition, lower is the CCT, higher is the loss of packaging efficiency due to the incorporation of zirconia. For a 90% ratio of zirconia, the packaging efficiency decrease of 16% for a 6500 K and 25% for a 4500K. The physical reason of the decrease of packaging efficiency, for a specific CCT, with the amount of ZrO_2 is certainly linked to the scattering effect of ZrO_2 that increase the backscattering of light, So less blue and yellow emission are extracted outside the device.

In addition of the ZrO_2 influence on the phosphor reduction and the packaging efficiency, the incorporation of zirconia has an influence of the color uniformity, $\Delta CCTD$, as shown in Fig. 9.

These results clearly show the quality and the limit of the model developed in this work. Higher than 7000K, within an reasonable numbers of ray used in the ray-tracing model, the

adequation between the model and the experimental result is not acceptable. But in the usual range of CCT (4500-6500K), the modeling results are in excellent agreement with the experimental results.

The Fig. 10. show the simulation results of the color uniformity for an average 6500K package, with different amount of ZrO_2 .

The variation of CCT is about 650K for an 6500K package without ZrO_2 . By adding ZrO_2 , with a maximum ZrO_2 ratio of 90%, the ΔCCTD is less than 100K, as seen in Fig. 11.

For a specific CCT, the ΔCCTD is clearly decreasing with the incorporation of zirconia. This effect is even more important for low CCT, because the scattering effect is already important due to the higher amount of YAG. At high CCT (with less amount of YAG) the decrease of ΔCCTD is still important.

Conclusion

An efficient optical model was developed and applied to the incorporation diffuse particle of zirconia into a hemisphere package containing YAG phosphors. The optical properties (chromaticity, packaging efficiency) can be estimated as a function of phosphor and ZrO_2 particles, through the calculation of effective radius, refractive index, absorption and conversion efficiency, in a range of 4500K to 6500K. In the same way, the amount of phosphor and zirconia can be calculated to obtain a targeted optical property in a hemisphere LED design.

The incorporation of zirconia particles allows clearly decreasing the amount of phosphor for an identical target CCT. The zirconia particles increase the pathway of the incident blue light inside the package, so increase the possibility for the blue beam to be absorbed by a phosphor particle.

In addition, the angular distribution of CCT is also diminished, and even almost inexistent for low CCT design. The yellow ring phenomenon is not revealed anymore. This is due to the scattering effect of zirconia, what spread in all the direction the blue and yellow light outside the hemisphere.

However, a trade-off has to be taken into account. While hitting a particle, a part of the blue beam is not reflected nor transfer radiatively to an emission phenomena. This last energy is transfer into thermal vibration and does not participate to the light extraction. Adding zirconia particles enhances this effect. So the trade-off of adding zirconia, that increase the light pathway, is the decrease of the packaging efficiency.

In addition, the scattering effect of the zirconia induces a more important backscattering, diminishing the amount of light extracted outside the device, that also get a negative influence on the global packaging efficiency.

In conclusion, adding micrometric zirconia particles may be suitable in the context of decreasing the amount of phosphor or in some applications where the CCT angular distribution is an important parameter, like indoor down-lighting.

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Figure Captions

Fig. 1. Example of simulated and experimental light scattering.

Fig. 2. Effective refractive index and particle radius as a function of ratio of ZrO_2 .

Fig. 3. a) Configuration of the experimental set-up, b) Examples of spectral measurements, c) Scheme of the blue and yellow extraction.

Fig. 4. Process of Optical Modeling.

Fig. 5. Effective Absorption coefficient and Conversion Efficiency.

Fig. 6. Hemisphere packaging device

Fig. 7. Chromaticity of selected hemisphere packaging samples.

Fig. 8. Packaging efficiency and Phosphor reduction as a function of ratio of ZrO_2 for various CCT.

Fig. 9. CCT as a function of angle, for various amount of ZrO_2 ratio.

Fig. 10. CCT as a function of angle, for an average 6500K package, with various amounts of ZrO_2 ratio.

Fig. 11. Packaging efficiency and ΔCCTD as a function ZrO_2 ratio, for an average 6500K package.

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